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AUTOMATED HPLC METHOD FOR LOW LEVEL POLYNUCLEAR AROMATIC HYDROCARBON (PAH) ANALYSIS OF DRINKING WATER.

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Polynuclear Aromatic Hydrocarbons are homologs of benzene in which three or more aromatic rings are joined in various configurations. Generally, they are characterized as being high melting point/high boiling point solids with low vapour pressures at ambient temperature and atmospheric pressure[1]. PAHs are relatively hydrophobic compounds which do not readily dissolve in water or water miscible solvents at high concentrations. PAHs are formed during heating, burning and incinerating processes involving carbonaceous materials. In nature PAHs are produced by combustion of organic matter under conditions of insufficient oxygen and/or low combustion temperature. Industrial PAH production is associated with coal/oil/gas burning power plants and combustion engines as well as steel manufacturing and petrochemical industries[2]. PAHs are major components of asphalt, coal tar and soot. Several members of this chemical class have been shown to be carcinogenic to animals and several are suspected carcinogens for man[3]. PAHs are of environmental concern because of their natural abundance, bioconcentration in fatty tissues, bioaccumulation along the food chain and carcinogenic activity.

PAHs have been extensively studied in stack gases, polluted air and food products[4,5]. More emphasis is being placed on the analysis of PAHs in drinking water due to their discovery in monitoring programs at select locations in Ontario. The implementation and expansion of sampling programs such as the Drinking Water Surveillance program (DWSP) and Municipal Industrial Strategy for Abatement (MISA) has necessitated the development of automated low level analytical techniques. A routine automated low level high performance liquid chromatography (HPLC) method was developed to analyse drinking waters for 17 individual PAHs with the most important ones for monitoring purposes being fluoranthene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene and indeno(123cd)pyrene. The World Health Organization (WHO) states the concentrations of these six representative PAHs should not exceed 200ng/L in drinking water[6]. This new routine analytical method increases production and data quality, and reduces detection limits and data interpretation time.



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The hydrophobic nature of the PAHs necessitated individual standard stock solutions be made up using 5% benzene in methanol at concentrations between 10 $\mu\text{g/mL}$ and 100 $\mu\text{g/mL}$ depending on the individual PAH's water solubility. These concentrations ensured complete solute dissolution and eliminated solute precipitation from solution upon refrigerated storage.

Wet chemical sample preparation involves liquid/liquid extraction followed by a three stage concentration and solvent exchange. Samples are extracted three times with dichloromethane using a roller apparatus and the subsequent extract dried through sodium sulphate. Extracts are then evaporated to dryness using rotovap apparatus/vortex evaporator/nitrogen blow-down and the solute resuspended in acetonitrile for instrumental analysis.

Instrumental analysis is done by reversed phase HPLC. Individual components are separated using a Vydac reversed phase C18 column and solvent gradient program. A programmable Perkin Elmer LS4 fluorescence detector is used to achieve the necessary detection limits to monitor PAHs at/or below World Health Organization drinking water guidelines.

Instrument retention times were consistent over time with coefficients of variation <0.3%. Height quantitation results were slightly better than area quantitation results with coefficients of variation approximately 5%. Fluorescence detector linearity was limited to a range of approximately 10E2 with some components such as anthracene and benzo(k)fluoranthene being less. Detector linearity ranges did however increase as the fluorescence source lamp aged and the detector became less sensitive.

Method spikes between 0.5 ng/L and 1000 ng/L were analysed to establish recoveries and reproducibility. High level spikes were diluted to established detector linearity ranges for proper quantitation. Method recoveries were comparable at all spike levels tested. Average method recoveries were > 75% for most PAHs with the exception of anthracene, benzo(a)pyrene and dimethylbenzo(a)anthracene. Anthracene losses are a direct result of evaporation during extract concentration. Benzo(a)pyrene and dimethylbenzo(a)anthracene losses appear to be related to the water

extraction stages of the method rather than evaporation steps. Method detection limits range from 1 ng/L for anthracene and benzo(k)fluoranthene to 50 ng/L for benzo(e)pyrene and chrysene. The detection limit for benzo(a)pyrene is 5 ng/L which is below the World Health Organization drinking water guideline of 10 ng/L.

Several areas for method modification and improvement are scheduled for investigation. Lower detection limits for some components and reduced analysis time may be achieved by further wavelength switching and gradient/flow modifications respectively. New extraction/concentration techniques (eg. Goulden Evaporator) could increase recoveries and analytical precision by limiting extract handling procedures. The addition of environmentally significant PAH derivatives such as nitroPAHs to the scan would enhance the Drinking Water Organics Section monitoring capabilities.

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